

V_K Centers and Recombination Luminescence in Rubidium Iodide and Sodium Iodide*

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V_K centers are introduced into both NaI and RbI by low-temperature irradiation of crystals containing electron-attaching impurities. These centers are identified by optical-absorption spectra and by the anisotropic absorption of oriented centers. V_K centers are stable in NaI below about 58°K, and in RbI below about 125°K. These temperatures permit an estimate of the thermal activation energy for migration of the I_2^- as 0.15 and 0.32 eV, respectively. Recombination of electrons with V_K centers in both crystals produces the "intrinsic" luminescence characteristic of the pure crystal. The connection with exciton states is discussed briefly.

I. INTRODUCTION

THE V_K center, or self-trapped hole, has been identified in several alkali halides of the NaCl structure.¹ This center is a molecular ion of the form X_2^- with an axis of symmetry along a $\langle 110 \rangle$ direction of the crystal, and is stable only at low temperatures, e.g., below $\sim 105^\circ\text{K}$ for KI. This defect is of particular interest as it consists only of a localized charge deficiency (a hole) with an associated lattice distortion, i.e., two neighboring halides are pulled together along a $\langle 110 \rangle$ direction. Recombination of an electron with a self-trapped hole results in excited states which are thus characteristic of the pure crystal lattice. The radiative decay of these states has been shown to be responsible for the intrinsic luminescence observed in several "pure" alkali halides at low temperatures.^{2,3}

The purpose of this paper is to report the observation of stable V_K centers in rubidium iodide and sodium iodide, and the luminescence resulting from the recombination of electrons with V_K centers.

II. EXPERIMENTAL METHODS

Crystals of nonactivated NaI and RbI, and activated crystals of RbI(Tl), RbI(Ag), NaI(Tl), and NaI(Eu) were obtained from Harshaw and Semi-Elements. Low-temperature irradiations and measurements of absorption spectra, emission spectra, and excitation spectra were performed with equipment and techniques described previously.² All measurements of emission spectra have been corrected for the monochromator-detector response function.

III. V_K CENTERS IN RUBIDIUM IODIDE

We identify the V_K center in RbI by its optical-absorption properties. In order to form stable V_K

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¹ C. J. Delbecq, W. Hayes, and P. H. Yuster, *Phys. Rev.* **121**, 1043 (1961).

² R. B. Murray and F. J. Keller, *Phys. Rev.* **137**, A942 (1965).

³ M. N. Kabler, *Phys. Rev.* **136**, A1296 (1964).

centers in relatively high concentration it is necessary to irradiate crystals containing an electron-trapping impurity. We have used both RbI(Tl) and RbI(Ag) for this purpose. Most of the experiments were performed with a crystal of RbI(Tl) from Semi-Elements. A flame photometer analysis gave the thallium content as 4×10^{-4} mole%. This crystal is referred to hereafter simply as RbI(Tl).

Irradiation of the RbI(Tl) at liquid-helium temperature (LHT) with 1.7-MeV electrons results in optical-absorption bands as shown in Fig. 1. The two most prominent bands peak at 405 and 793 $m\mu$. A distinct shoulder on the long-wavelength side of the 405- $m\mu$ band is due to a band whose peak is estimated to lie near 560 $m\mu$. A very weak absorption is peaked near 1.1 μ . The peak wavelengths and relative intensities of these four bands are nearly identical to the properties of the V_K bands in KI, as identified by Delbecq *et al.*¹ and Hersh.⁴ Another prominent radiation-induced band occurs at 307 $m\mu$, and strong absorption is induced below about 250 $m\mu$. These bands have not been identified or studied further. The principal bands discussed above are also introduced by irradiation at

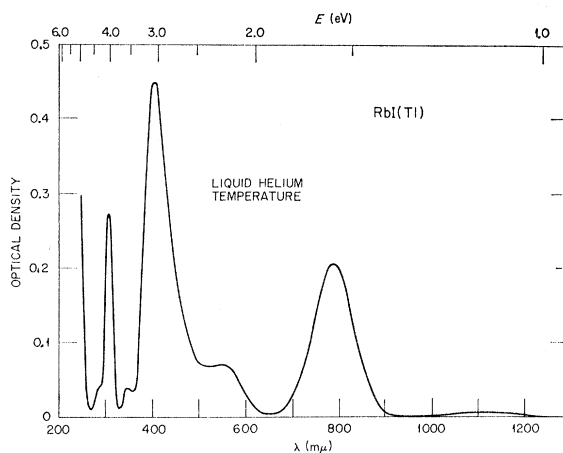


FIG. 1. Radiation-induced absorption spectrum in RbI(Tl). The crystal was irradiated and the spectrum was measured at LHT.

⁴ H. N. Hersh, *J. Chem. Phys.* **31**, 909 (1959).

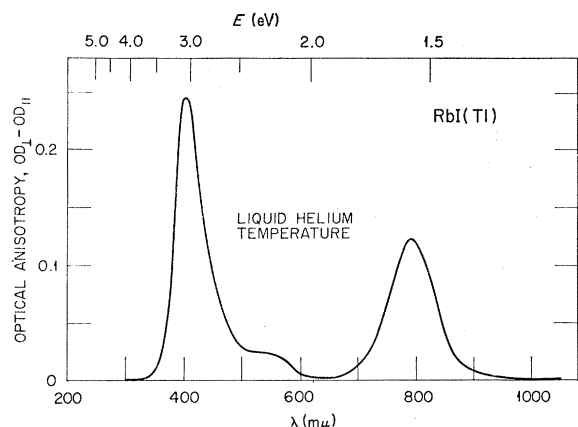


Fig. 2. Optical anisotropy induced by bleaching the crystal of Fig. 1 with linearly polarized light ($\lambda=405\text{ m}\mu$), with electric vector parallel to a $\langle 110 \rangle$ axis. Crystal was bleached and spectrum was measured at LHT.

liquid-nitrogen temperature (LNT), although the structure is somewhat obscured by the very strong F band whose peak occurs at $731\text{ m}\mu$. A crystal of RbI(Tl) exposed at LNT to the same radiation dose as that of Fig. 1 exhibits an F -band optical density of 1.2, and a $405\text{-m}\mu$ peak of optical density 0.43. It is noted that the F band is not even observed in Fig. 1. Thus, in RbI(Tl), the production efficiency for F centers is enormously greater at LNT than at LHT.

As a further check on the identity of the I_2^- ion, the optical anisotropy of the bands in Fig. 1 was studied. After measuring the absorption spectrum of Fig. 1, the crystal was bleached with linearly polarized light ($\lambda=405\text{ m}\mu$) whose electric vector was parallel to the $[011]$ direction with propagation vector along $[100]$.⁵ A distinct dichroism was readily induced, and the optical anisotropy was measured and is shown in Fig. 2. Optical anisotropy is here defined as $OD_1 - OD_{11}$, where OD_1 is the optical density measured with polarized light whose electric vector is perpendicular to that of the bleaching light, and OD_{11} is measured with electric vector parallel to that of the bleaching light. The anisotropic-absorption spectrum of Fig. 2 is very similar to that of the I_2^- ion in KI, as reported previously.^{1,4}

TABLE I. Optical anisotropy produced by bleaching with polarized light.^a

Centers with optical dipole moments oriented parallel to	Is anisotropy produced by bleaching with light polarized parallel to $[001]$?	Is anisotropy produced by bleaching with light polarized parallel to $[011]$?
$\langle 100 \rangle$	yes	no
$\langle 110 \rangle$	yes	yes
$\langle 111 \rangle$	no	yes

^a Taken from W. D. Compton and C. C. Klicik, Phys. Rev. **110**, 349 (1958).

⁵ In all bleaching experiments and in all measurements of dichroic absorption, the propagation vector was along the $[100]$ direction.

Additional information on the symmetry axis of the center responsible for the spectrum of Fig. 2 was obtained in a later experiment in which RbI(Tl) was irradiated at LHT and then bleached at $405\text{ m}\mu$ with light polarized parallel to the $[001]$ direction. A dichroic absorption was induced and the anisotropic absorption spectrum was that of Fig. 2. These results can be compared with Table I, which summarizes whether or not an optical anisotropy will be induced for centers with a given symmetry axis. Since an anisotropic absorption was produced in both bleaching experiments described, these results indicate a $\langle 110 \rangle$ symmetry axis.

Irradiation of a crystal of RbI(Ag) with 1.7-MeV electrons at LHT introduces bands at 405 and $\sim 793\text{ m}\mu$. A weak F band occurs also on the short-wavelength side of the $793\text{-m}\mu$ band. Bleaching with $[011]$ polarized light at $400\text{ m}\mu$ produces an anisotropic absorption which is the same as that of Fig. 2.

In view of the foregoing results, we conclude that V_K centers are produced in rubidium iodide upon irradiation at LHT, and are responsible for the aforementioned absorption bands.

In order to perform some of the luminescence experiments to be described later, it is necessary to know at what temperatures V_K centers are thermally stable. The stability of the I_2^- against reorientation was measured by recording the optical anisotropy due to oriented V_K centers (oriented along $[011]$) in RbI(Tl) while the crystal was slowly warmed above LNT (heating rate $1.7^\circ\text{K per min}$). The results are plotted in Fig. 3, showing a maximum slope in the neighborhood of 100°K . In a subsequent experiment, the absorption coefficient of V_K centers at $405\text{ m}\mu$ was followed as a function of temperature, and was found to decay at a maximum rate at about 125°K . This may be compared, for example, with the analogous temperature of 105°K

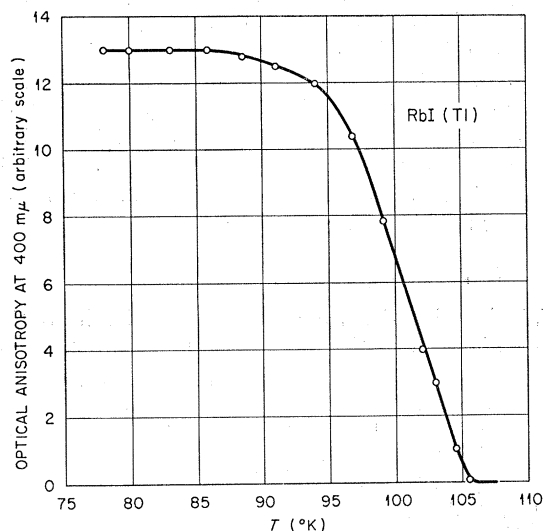


Fig. 3. Optical anisotropy at $400\text{ m}\mu$, due to oriented I_2^- in RbI(Tl), as the crystal is warmed at a rate of $1.7^\circ\text{ min}^{-1}$.

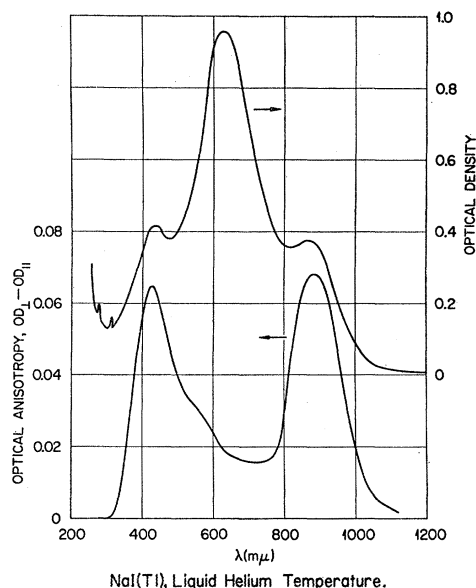


FIG. 4. (Top)—Radiation-induced absorption spectrum of NaI(Tl). The crystal was irradiated and the spectrum was measured at LHT. (Bottom)—Anisotropic-absorption spectrum resulting from bleaching with linearly polarized light ($\lambda=430\text{ m}\mu$), electric vector along a $\langle 110 \rangle$ axis of crystal.

in potassium iodide. Previous studies^{6,7} of the thermally excited reorientation and diffusion of V_K centers in KI showed that V_K motion is characterized by a jump frequency of the form $S \exp(-E/kT)$, where the activation energy E is 0.27 eV. If we make the reasonable assumption that the pre-exponential factor S is nearly the same for I_2^- in RbI as in KI, then the activation energy for V_K motion in RbI is approximately 0.32 eV.

It is interesting to note that the irradiation of RbI(Tl) did not produce any measurable thallium perturbation bands,⁴ whereas they were clearly introduced by the irradiation of NaI(Tl). The band at $307\text{ m}\mu$ of Fig. 1 is considerably wider than a thallium perturbation band.

IV. V_K CENTERS IN SODIUM IODIDE

Irradiation of a crystal of NaI(Tl) (3×10^{-3} mole % thallium) at LHT with 1.7-MeV electrons results in an absorption spectrum shown at the top of Fig. 4. Bleaching at LHT with linearly polarized light ($430\text{ m}\mu$) whose electric vector was parallel to $[011]$ results in dichroic absorption, and the anisotropic-absorption spectrum is shown at the bottom of Fig. 4. Peaks in the anisotropic-absorption spectrum occur at 880 and $432\text{ m}\mu$. Similar experiments in NaI(Eu) give an anisotropic-absorption spectrum which is indistinguishable from that of Fig. 4. Furthermore, bleaching of irradiated NaI(Tl) at LHT with linearly polarized light ($430\text{ m}\mu$) whose electric vector was parallel to the $[001]$ direction

produced a similar anisotropic absorption. The similarity of these spectra to the anisotropic absorption of I_2^- in KI and RbI, and the identification of the symmetry axis as $\langle 110 \rangle$ from Table I, leads to the conclusion that I_2^- is stable in NaI at LHT.

The thermal stability of I_2^- in NaI was examined by measuring the anisotropic absorption at $875\text{ m}\mu$ from oriented V_K centers in NaI(Eu) as the crystal was slowly warmed above LHT. The anisotropy was found to decrease rapidly above 48°K , the maximum rate of decrease occurring at 52°K . A second feature of the absorption spectrum which can be used to monitor the instability of self-trapped holes is associated with several rather sharp bands in the near ultraviolet which occur upon irradiation of NaI(Tl). Similar bands have been reported in irradiated KI(Tl) by Hersh,⁴ who labeled them as the "thallium perturbation bands" P_1 , P_2 , and P_3 , occurring at $\lambda=305$, 264, and $257\text{ m}\mu$, respectively. Hersh showed that these bands in KI(Tl) are apparently due to the perturbation of the Tl^+ ion by a trapped defect. The P_1 and P_3 bands are very likely due to trapping of a hole at Tl^+ , as they increase abruptly in KI(Tl) at about 105°K , where the self-trapped holes begin to diffuse through the lattice. In the case of NaI(Tl), we find similar radiation-induced bands at 312, 277, and $257\text{ m}\mu$, and we note that the 312- and $257\text{-m}\mu$ bands increase in intensity abruptly just below 60°K . By analogy with KI(Tl), we believe that the three bands at 312, 277, and $257\text{ m}\mu$ are P_1 , P_2 , and P_3 bands, respectively, and that the P_1 and P_3 bands are due to trapping of a hole at Tl^+ .

Considering the temperature dependence of the anisotropic absorption, and the behavior of the P bands, we conclude that V_K centers become mobile in NaI at a temperature of about 58°K , to be compared with 105°K in KI. On this basis, the thermal activation energy for motion of I_2^- ions in NaI is approximately 0.15 eV.

It is noted in the top of Fig. 4 that the radiation-induced absorption spectrum of NaI(Tl) contains a prominent band whose peak wavelength occurs at $620\text{ m}\mu$ at LHT. This band is apparently not associated with absorption in V_K centers, as there is no evidence of a prominent peak at this wavelength in the anisotropic-absorption spectrum. Furthermore, this band is stable upon heating to LNT, and is in fact introduced by irradiation at LNT (the peak wavelength at LNT is $\sim 630\text{ m}\mu$). Studies of the excitation spectrum of luminescence, which is attributed to the recombination of electrons with V_K centers, described below, leads to the conclusion that the $620\text{-m}\mu$ band is associated with an electron-excess center. It is not to be identified as the F band, however, as we have produced F centers by prolonged irradiation of nonactivated NaI at room temperature, and find the peak wavelength of the F band at LNT to be $596\text{ m}\mu$. Furthermore, irradiation of "pure" NaI at LHT with a dose equal to that of Fig. 4 produced an extremely small F -band absorption (OD

⁶ F. J. Keller and R. B. Murray, Phys. Rev. Letters **15**, 198 (1965).

⁷ F. J. Keller and R. B. Murray, Phys. Rev. **150**, 670 (1966).

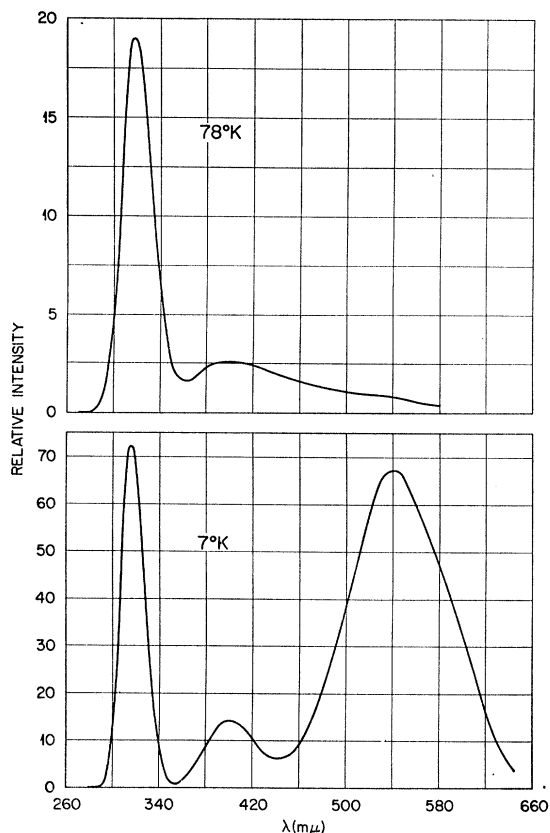


FIG. 5. Emission spectra from nonactivated RbI (Harshaw) during x-ray excitation at 7 and 78°K. The spectra have been corrected for the monochromator-detector response function. Ordinates are directly comparable.

=0.08), not at all comparable to the 620-m μ band of Fig. 4. A study of the excitation spectrum of irradiated KI(Tl) by Hadley and co-workers⁸ showed that there were excitation peaks associated with an electron-excess center, in the 500–700-m μ range, and these peaks are probably associated with the Tl⁰ center. In view of the foregoing, we attribute the 620-m μ band to a radiation-induced electron-excess center associated with the thallium impurity, and, by analogy with KI(Tl), we tentatively identify it as the Tl⁰ center.

V. RECOMBINATION LUMINESCENCE IN RbI

The luminescence-emission spectrum from non-activated RbI during stimulation by x rays is shown in Fig. 5. There are three principal emission bands which are characteristic of the host material, and their peak wavelengths at LHT are located at 316, 400, and 540 m μ . The 316-m μ band is well resolved from the two longer wavelength bands, and it persists to relatively high temperatures. The relative intensity of this band (measured as its area) is shown as a function of temperature in Fig. 6. If we assume that the decrease in intensity

⁸ W. B. Hadley, S. Polick, R. G. Kaufman, and H. N. Hersh, *J. Chem. Phys.* **45**, 2040 (1966).

above ~50°K is due to a simple competition with a nonradiative process, then the luminescence efficiency should be described by a function of the form

$$\eta = \frac{P_r}{P_r + \nu \exp(-E/kT)}, \quad (1)$$

where P_r is the radiative-transition probability (assumed independent of T), ν is a constant, and E is the thermal activation energy required to reach the nonradiative state. An appropriate plot of the data of Fig. 6 above 50°K shows that these data are well described by such a function, with $E=0.05$ eV.

The intensity of the 540-m μ band decreases with increasing temperature above 7°K, and appears only as a shoulder on the 400-m μ band at 40°K and above. The 400-m μ band increases above 7°K to a maximum near 50°K and then decreases rapidly. As shown in Fig. 5, both of these bands are quite weak at LHT compared to the 316-m μ band.

The spectra of Fig. 5 were obtained with a RbI crystal obtained from Harshaw; this crystal exhibited no impurity absorption bands in the near-infrared to near-ultraviolet region. The three emission bands observed at LHT have also been seen by Ramamurti and Teegarden⁹ during ultraviolet stimulation of "pure" RbI with 7.7-eV photons. However, we do not observe

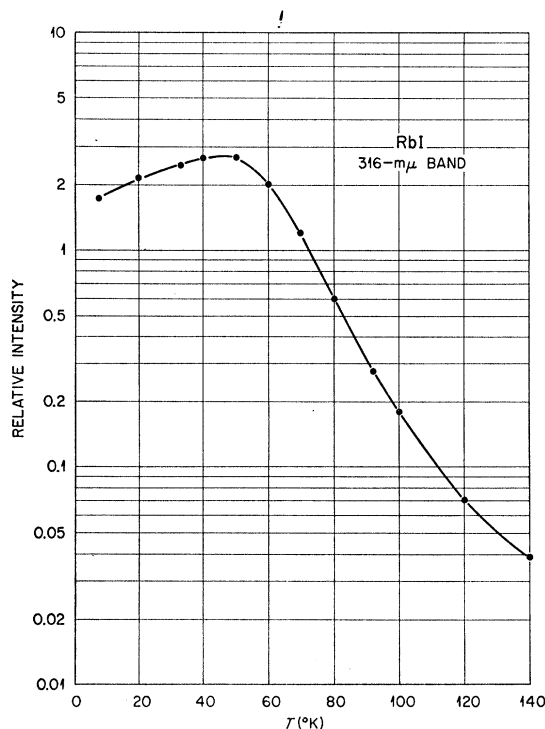


FIG. 6. Temperature dependence of the 316-m μ band in RbI (Harshaw) during x-ray excitation. Data points represent the area under the 316-m μ band.

⁹ J. Ramamurti and K. Teegarden, *Phys. Rev.* **145**, 698 (1966).

any evidence that the 540-m μ emission is composed of two bands, as is indicated in their work.

A crystal of nonactivated RbI from Semi-Elements was x rayed at LHT, and the emission spectrum was composed of the same three bands as in Fig. 5. This crystal showed a very weak absorption at 280 m μ , which coincides with the peak wavelength of the thallium *A* band. The observed band corresponds to a thallium concentration of about 1×10^{-5} mole%. Similarly, the x-ray excited emission spectrum of RbI(Tl) at 7°K contained the same three bands, but no other bands which might be expected from thallium luminescence. In the spectra from both of these crystals, the longer wavelength bands at 400 and 540 m μ were somewhat weaker relative to the 316-m μ band, in comparison to the spectrum at the bottom of Fig. 5. This effect may be due to optical absorption in the longer wavelength region arising from V_K centers produced during the irradiation, as the V_K absorption spectrum overlaps the long-wavelength bands (see Fig. 1). Experiment shows that V_K centers are produced and stabilized at LHT by irradiation of both of these crystals. A similar, but more pronounced, change in relative intensities is observed in the luminescence from crystals containing a relatively high density of V_K centers (see next paragraph).

In order to determine whether the emission bands of Fig. 5 are due to ($e^- + V_K$) recombination, experiments were performed with oriented V_K centers. The method is the same as that described previously² and is discussed here only briefly. A RbI(Tl) sample was irradiated at LNT, producing the absorption bands of Fig. 1 plus a prominent *F* band. The crystal was cooled to LHT, and optical excitation with *F* light produced an emission containing the three bands of Fig. 5, but with weaker intensity in the two long-wavelength bands relative to the 316-m μ band. This difference in the emission spectrum is attributed to self-absorption by the prominent V_K bands resulting from the high-intensity Van de Graaff irradiation. Light at 316 and 540 m μ was found to be unpolarized. V_K centers were then oriented by bleaching with linearly polarized 400-m μ light whose electric vector was parallel to the [011] axis. After orientation, the emission bands at 316 and 540 m μ were found to be linearly polarized with the electric vector of the 540-m μ band parallel to the electric vector of the bleaching light, and the 316-m μ band perpendicular. If we assume¹⁰ that the orienting transition is σ polarized (i.e., the transition occurs with electric vector parallel to the molecular axis), then the 316-m μ band is polarized with electric vector parallel to the V_K axis, and the 540-m μ band is polarized with electric vector perpendic-

ular to the V_K axis. We have not attempted to measure a polarization in the 400-m μ band as it is quite weak and it overlaps almost precisely the strongest V_K absorption band which is, of course, dichroic after orientation of the V_K centers. Figure 2 shows that there is a weak dichroic absorption at 540 m μ , which could produce an apparent polarization in the 540-m μ luminescence even if the emission were unpolarized. This effect, however, is in the opposite direction from the polarization observed, and serves only to decrease the magnitude of the measured polarization.

Although we were not able to measure a polarization at 400 m μ , we believe that this band is also due to ($e^- + V_K$) recombination by virtue of its persistence in all of the x-ray excited spectra, its occurrence upon stimulation in the *F* band of irradiated RbI(Tl), and its observation upon ultraviolet excitation.⁹

The excitation spectrum of the 316-m μ band was measured in irradiated RbI(Tl) at LNT, and was found to have a peak at 730 m μ (corresponding to the *F* band) and another maximum near 1.1 μ . This behavior is quite similar to that of KI(Tl). The long-wavelength peak is presumed to arise from the optical excitation of electrons from Tl^0 . Electron-trapping processes in KI(Tl) have been discussed in detail by Hadley and co-workers.⁸ We conclude that optical stimulation in the *F* band or the 1.1- μ band releases electrons which can recombine with self-trapped holes. This recombination results in excited states which decay radiatively to produce the 316- and 540-m μ bands, as shown by the polarized luminescence, and probably produces the 400-m μ emission.

It is interesting that optical stimulation of irradiated RbI(Tl) does not produce any luminescence which can be identified with thallium, as is the case in KI(Tl) and NaI(Tl) (see next section). The absence of thallium luminescence is consistent with the previous observation that no thallium perturbation bands were produced by irradiation of RbI(Tl). In both KI(Tl) and NaI(Tl), low-temperature irradiation produces the perturbation bands, and stimulation of electron-excess centers produces thallium luminescence by the mechanism $e^- + Tl^{++} \rightarrow (Tl^+)^*$. Apparently the Tl^+ ion does not serve as an effective hole trap in RbI, but it does serve as an electron trap, as indicated by the formation of stable V_K centers in RbI and the stimulability in the long-wavelength region ($\sim 1.1 \mu$). We must note, however, that the RbI(Tl) crystal used in these experiments was of relatively low Tl concentration. It is possible that hole trapping at Tl^+ sites would be observed in a crystal of considerably higher Tl content.

VI. RECOMBINATION LUMINESCENCE IN NaI

Luminescence from nonactivated NaI at low temperatures has been studied by Van Sciver,¹¹ who observed a

¹⁰ Optical experiments alone cannot determine whether the orienting transition is σ or π polarized. The work of Delbecq, Hayes, and Yuster, Ref. 1, utilizing spin resonance, shows that the V_K bands are σ polarized in LiF, KCl, and KBr. Patten and Marrone [Phys. Rev. 142, 513 (1966)] have shown that the V_K bands are largely σ polarized in NH₄Br. We therefore assume the V_K bands of RbI to be predominantly σ polarized.

¹¹ W. J. Van Sciver, Phys. Rev. 120, 1193 (1960); IRE Trans. Nucl. Sci. NS-3, 39 (1956).

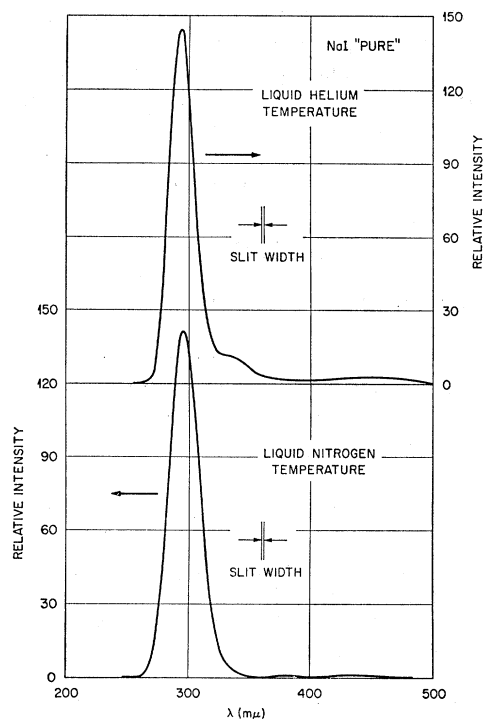


FIG. 7. Emission spectra from nonactivated NaI (Harshaw) at LNT and LHT during x-ray excitation. The spectra have been corrected. Ordinates are directly comparable. The area under the band at LNT is about 20% greater than that at LHT owing to the greater width.

prominent emission band at 295 $m\mu$ upon excitation by ultraviolet light of energy equal to or greater than that of the fundamental absorption band. This same luminescence was also observed in NaI upon excitation by gamma rays or alpha particles. The luminescence spectrum from nonactivated NaI at LNT and LHT has been measured in this work during x-ray excitation, and is in agreement with the previous studies. X-ray-excited spectra are shown in Fig. 7. The luminescence intensity as a function of temperature is very similar in shape to that of Fig. 6. The maximum intensity occurs at about 70°K and decreases by 20% in cooling to 7°K. The intensity decreases by a factor of 11 in warming from 70 to 273°K, and the intensity is described in this temperature region by Eq. (1) with $E=0.06$ eV. The observed temperature dependence is in good agreement with previous measurements¹² of the scintillation efficiency of nonactivated NaI as a function of temperature.

Irradiation of NaI(Tl) at LHT results in an absorption spectrum, as shown at the top of Fig. 4. If the crystal is illuminated with 620- $m\mu$ light, the luminescence spectrum is composed of the 295- $m\mu$ band plus additional bands at 328 and 422 $m\mu$. These latter two bands are closely analogous to known thallium-emission bands which occur in KI(Tl) at LHT (see Ref. 2 and

references therein), and are therefore presumed to arise from thallium in NaI(Tl). The 295- $m\mu$ band in this spectrum appears to be double, as there is a distinct sharp valley at 288 $m\mu$, arising from absorption in the thallium A band. If the V_K centers are oriented by bleaching at 430 $m\mu$, the 295- $m\mu$ band is found to be linearly polarized, and the electric vector is parallel to the electric vector of the bleaching light. If we assume that the orienting transition is σ polarized, then the electric vector of the emitted light is perpendicular to the V_K axis.

A similar experiment with NaI(Eu) at LHT gave the same result for the polarization effect.

VII. DISCUSSION

Measurements of the thermal activation energy for the motion of V_K centers in the three alkali iodides NaI, KI, and RbI show that the activation energy increases with increasing size of the cation. This is the behavior which one expects intuitively, as a close spacing between halide ions should make it relatively easy for the self-trapped hole to move from one site to another. For these three alkali iodides, the thermal activation energy for V_K motion increases monotonically with nearest-neighbor separation distance between I^- ions, as shown in Table II.

We turn now to the recombination luminescence. Electron spin-resonance experiments have shown that the self-trapped hole is a property of the pure crystal lattice, i.e., it is not adjacent to another defect such as an impurity ion or a vacancy. If an electron recombines with a V_K center to produce an excited state, then this state is one which is a property of the pure crystal lattice and which has the normal charge. It is, of course, a nonconducting state as the electron and hole are bound. It must be noted that these are states in which the lattice retains the axis of symmetry characteristic of the I_2^- , as shown by the polarized luminescence experiments. Thus, the excited state must be one in which the captured electron is confined to an orbital about the V_K center, and this configuration is retained during the lifetime of the radiative state, i.e., the nuclear coordinates do not relax to restore cubic symmetry about an excited I^- ion. These states are, therefore, not the same as exciton states populated by

TABLE II. Data on V_K centers in three iodides.

Crystal	Principal V_K bands ($m\mu$)	Nearest-neighbor iodine separation (\AA)	V_K thermal activation energy (eV)	References
NaI	432, 880	4.57	≈ 0.15	This work
KI	400, 800	4.99	0.27	a, b
RbI	405, 793	5.18	≈ 0.32	This work

¹² W. J. Van Sciver and L. Bogart, IRE Trans. Nucl. Sci. NS-5, 90 (1958).

^a Reference 6.

^b Reference 7.

optical absorption in the fundamental band. The (e^-+V_K) states correspond instead to a "self-trapped" or "relaxed" exciton.

In connection with the above, we are led to ask whether exciton states populated optically (by excitation in the fundamental band) relax to trapped-exciton states of the (e^-+V_K) configuration. The mechanism envisioned is one in which the exciton state is initially created in cubic symmetry, followed by a relaxation of nuclear coordinates to an (e^-+V_K) state. Evidence that this relaxation process does occur in some cases is found by a comparison of the luminescence-emission spectra resulting from excitation in the fundamental band with the emission spectra from (e^-+V_K) excited states created by recombination events: For example, Van Sciver¹¹ has observed ultraviolet excitation of the 295-m μ emission band in NaI by light in the fundamental band. The low-energy emission band (371 m μ) of KI has been observed by stimulation in the fundamental band,¹³ but the high-energy band (300 m μ) is excited only by ultraviolet light of higher energy. The low-energy emission band of KBr (546 m μ) is stimulated by ultraviolet light in the region of the exciton doublet, whereas the high-energy band (280 m μ) is excited only by higher energy photons.¹⁴ Thus, in these cases, the low-energy (e^-+V_K) emission bands (and the only band of NaI) are excited by stimulation in the fundamental band. We note, however, that there are (e^-+V_K) states which are not populated by fundamental band excitation, e.g., the high-energy emission bands in KI and KBr. Conversely, there are radiative states populated by fundamental band excitation which are not reached by (e^-+V_K) recombination. In KI, we have observed that ultraviolet excitation in the fundamental band at LHT excites a luminescence band at 410 m μ , in contrast to the (e^-+V_K) luminescence at 300 and 371 m μ . The latter bands are excited by ultraviolet excitation of energy higher than the fundamental band. The 410-m μ band is temperature dependent, decreasing rapidly near 60°K, and is not resolved at LNT. (In view of the temperature dependence, this band probably does not contribute to the longer wavelength photoluminescence reported by Teegarden¹⁵ at 113°K.) Ramamurti and Teegarden⁹ have observed that stimulation of RbI at 10°K by ultraviolet light in the fundamental band excites a prominent emission at 470 m μ ; this band is absent in ultraviolet stimulation at higher energies, and it is absent in the x-ray excited spectrum of Fig. 5. Furthermore, it is not observed in the (e^-+V_K) recombination luminescence reported here. Thus, it appears that there is not a simple one-to-one correspondence between all

exciton states excited optically and those states formed by (e^-+V_K) recombination.

The identification of the electronic states involved in the (e^-+V_K) center has been suggested by Kabler³ in terms of states of the X^-X^- molecule. The ground state is expected to be a ${}^1\Sigma_g^+$ state. Electric dipole transitions are allowed from ${}^1\Sigma_u$ or ${}^1\Pi_u$ excited states, the ${}^1\Sigma_u \rightarrow {}^1\Sigma_g^+$ transition being σ polarized and the ${}^1\Pi_u \rightarrow {}^1\Sigma_g^+$ transition π polarized. In the emission spectra of both KI and RbI, the high-energy band is σ polarized and the low-energy band is π polarized,¹⁵ so that it is reasonable to assign these transitions to ${}^1\Sigma_u \rightarrow {}^1\Sigma_g^+$ and ${}^1\Pi_u \rightarrow {}^1\Sigma_g^+$, respectively. A similar situation exists in KBr. In NaI only the π -polarized transition is observed, presumably from the ${}^1\Pi_u \rightarrow {}^1\Sigma_g^+$ transition. A possible interpretation for the observed properties of the emission bands and their temperature dependence is given by the work of Wood,¹⁶ who considers excited states of the (e^-+V_K) configuration. Taking into account the "noncrossing rule" for states of the same symmetry, he suggests that the lowest excited state (${}^1\Pi_u$) should be one with the electron in a very diffuse orbital about the V_K center with a correspondingly long lifetime against radiative decay, and that the higher energy ${}^1\Sigma_u$ state should retain a highly localized character with a short lifetime. This suggestion is in fact borne out for the cases of KI and KBr where the lifetimes of the high-energy states are $\sim 10^{-9}$ and 5×10^{-9} sec, respectively, and for the low-energy states 2×10^{-6} and 7×10^{-5} sec.^{17,18} The lifetime associated with the 540-m μ band in RbI is also anomalously long, $\sim 7 \times 10^{-6}$ sec, and the lifetime of the 316-m μ luminescence is shorter than 5×10^{-9} sec.¹⁹ On the basis of the configuration coordinate diagram proposed,¹⁶ the decreasing luminescence efficiency at higher temperatures results from thermal excitation from the bound states of the (e^-+V_K) to conduction band states or directly to the ${}^1\Sigma_g^+$ ground state. It does not seem possible to explain the increasing luminescence efficiency at very low temperatures in the 316-m μ band of RbI or the 295-m μ band of NaI, other than to speculate that the radiative states are being populated thermally from other excited states of long radiative lifetimes. In connection with this increasing luminescence efficiency, we must be careful to note that the measurements shown in Fig. 6, and similarly for NaI, were taken during x-ray excitation, and the temperature dependence arises not only from the radiative-transition probability of the excited states involved, but also from the production efficiency of V_K centers and the probability of recombination to form an (e^-+V_K) state. We

¹⁵ These statements assume that the orienting transition is σ polarized, as discussed previously.

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¹⁸ M. N. Kabler, Bull. Am. Phys. Soc. **11**, 246 (1966).

¹⁹ D. Fröhlich (private communication).

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have no guarantee that these processes are temperature independent; such effects might well contribute to the observed temperature dependence.

Another interesting feature of the recombination luminescence is the fact that NaI exhibits only one prominent emission band in contrast to the two bands of KI and RbI (possibly three). The presence of only a

π -polarized band in NaI indicates that the ${}^1\Sigma_u$ state is not populated in the recombination or else it is not stable. Wood¹⁶ suggests that the minimum in the potential energy of the ${}^1\Sigma_u$ state may occur near the crossover point of the various excited levels, such that the ${}^1\Sigma_u$ state empties into the lower energy ${}^1\Pi_u$ state and only this emission is observed.

Some Properties of Defects Produced by Ionizing Radiation in KCl between 80 and 300°K*

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A number of experimental techniques have been combined to study radiation-induced defects that are complementary to *F* centers. One series of experiments, in which the resistance to dislocation motion due to interstitial centers was monitored by means of flow-stress changes, indicated that the centers produced by irradiation at 80°K and warming in the dark to room temperature were less effective barriers than were those produced by irradiation above 150°K. In a second series of experiments, measurement of vacancy-center bleaching rates indicated that defects produced by 80°K irradiation and warming to room temperature were much more easily bleached out than were those created by irradiation above 150°K. These results appeared to be correlated with changes in the ultraviolet absorption spectra where, for liquid-nitrogen irradiation and warming, the main absorption band appeared near 228 nm, whereas, for irradiation above 150°K, the main absorption appeared near 190 and 215 nm. The peak of the latter band moved to shorter wavelengths for higher irradiation temperatures. The results may be explained by assuming that interstitial clusters, together with vacancy centers, are produced by ionizing radiation, and that the clusters are of different sizes, depending upon irradiation temperature. There is also some evidence that trace impurities of concentration in the points per million (ppm) range influence the clustering process.

I. INTRODUCTION

ONLY recently has the role of interstitials in the radiation-damage processes of the alkali halides been appreciated. In fact, the existence of interstitials in irradiated alkali halides was not established at all until ESR results published in 1958 showed¹ that, for temperatures below about 55°K, the *H* center, an interstitial center,² was produced by radiation. As a result of this work, it was concluded³ that vacancy-interstitial pairs, Frenkel defects, were the predominant imperfections produced by radiation in the alkali halides at low temperatures. Later, Nadeau⁴ was able to postulate from a comparison of optical-absorption and flow-stress

measurements that interstitial centers were produced even in the case of room-temperature irradiation. More recent experiments⁵⁻⁷ have tended to confirm this hypothesis and to support the idea that Frenkel-pair production occurs under ionizing radiation at all temperatures.

Even though we now believe that Frenkel pairs are produced by radiation at all temperatures, the marked differences in damage rates when samples contain impurities or when they are irradiated at different temperatures⁸⁻¹² must still be accounted for. These differences could be due to either a temperature and impurity dependence of the production mechanism or mechanisms¹³ or to defect recombination processes.

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² For the purposes of this paper we use "interstitial center" as a generic term to cover all defects made up predominantly of interstitial halide, such as single interstitial ions or atoms, molecule ions containing more than one interstitial, etc. Similarly, we define "vacancy centers" as defects made up predominantly of negative-ion vacancies, such as *F*, *F'*, α centers, and *F*-aggregate centers.

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